

Fabricating colloidal crystals and construction of ordered nanostructures

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Abstract Colloidal crystals of polymeric or inorganic microspheres are of extensive interest due to their potential applications in such as sensing, optics, photonic bandgap and surface patterning. The article highlights a set of approaches developed in our group, which are efficient to prepare colloidal crystals with ordered voids, patterned colloidal crystals on non-planar surfaces, heterogeneous colloidal crystals of different building blocks, colloidal crystals composed of non-spherical polyhedrons, and colloidal crystals of non-close-packed colloidal microspheres in particular. The use of these colloidal crystals as templates for different microstructures range from nanoscale to micron-scale is also summarized.

Keywords Colloidal crystal · Nanostructure · Surface patterning

Introduction

Colloidal crystals of ordered microspheres represent a new class of advanced materials. For example, they can be used as scaffolds of highly ordered macroporous materials [1–6] and high-strength ceramics [7, 8]. Due to the novel light diffraction and photonic bandgap properties, colloidal crystals

are also promising candidates for constructing devices such as optical filters and switches [9, 10], chemical and biochemical sensors [11–13], and photonic chips [14, 15]. Various self-assembly techniques based on gravity sedimentation [16–18], electrostatic interaction [19–21], and capillary force [22–25] have been developed to form colloidal crystals on different substrates, including the flow-cell methods [26], vertical deposition [27–29], micromolding in capillaries (MIMIC) [30] and so on. Although the existing methods allow fabrication of colloidal crystals with close-packed structures, efficient approaches to form high-stability and large scale colloidal crystals of different structures are still demanded. On the other hand, introducing ordered microstructures within colloidal crystals is of particular importance for preparation of optical devices.

Recently, we have developed a number of methods to organize polymeric, inorganic, even composite microspheres [31–39] into various structures, generating various properties and functions. Using these methods, various of colloidal crystals with different structures have been prepared, including colloidal crystals with ordered voids [40] and two- or three-dimensional (2D or 3D) patterned arrays [41, 42], colloidal crystals on non-planar surfaces, heterogeneous colloidal crystals of different building blocks [42], colloidal crystals composed of non-spherical polyhedrons [43], and particularly colloidal crystals of non-close-packed colloidal microspheres [44]. Application of these colloidal crystals as templates for different structures range from nanoscale to micron-scale has also been introduced [43, 45–47].

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Fabricating new colloidal crystals of different structures

Colloidal crystals have attracted extensive interest due to their potential applications in fields, such as optics [48, 49], photonics [50], sensing [11, 51], and surface patterning. Although a large number of methods have been developed to control the size, structure, and crystalline orientation of colloidal crystals, challenges still exist in introducing some specific microstructures into them for their promising device applications.

Stable colloidal crystal chips and non-spherical colloidal crystals

Combining the vertical deposition with the MIMIC method, we have demonstrated a versatile procedure of fabricating high-quality stable colloidal crystal chips [38, 45]. Figure 1I, II schematically outlines the procedure. When two substrates were put in contact and vertically placed in the dispersions of microspheres, the dispersions were sucked in between them through capillary force. During the water evaporation, microspheres crystallized between the two substrates from the top to the bottom along the arrow direction

(Fig. 1I). A convective transportation of microspheres towards the upper crystallized microspheres was driven by the continuous flow of the dispersion, which was caused by the water evaporation and the capillary force between the substrates. After water evaporated completely, stable colloidal crystals were formed in between the two substrates. Figure 2I shows typical scanning electron microscopy (SEM) image of the colloidal crystals obtained by two-substrate vertical deposition.

The confinement of the two substrates renders colloidal crystal chips rather mechanically stable. Accordingly, we have developed an alternative approach towards non-spherical colloidal crystals (NSCCs). First, colloidal crystal chips constructed from low-cross-linked polystyrene beads were prepared by two-substrate vertical deposition. Second, these colloidal crystal chips were pressed at the temperature of slightly below the glass transition temperature (T_g) of the polymer colloids (Fig. 1III). After thermal-pressing, polymer beads were transformed into polyhedrons (quasi rhombic dodecahedrons as illustrated by the model in Fig. 1IV), and NSCCs were obtained. In our experiments, heating procedure only made polymer spheres tend to transform, while the high pressure

Fig. 1 Schematic illustration of two-substrate vertical deposition and procedure used to prepare NSCCs

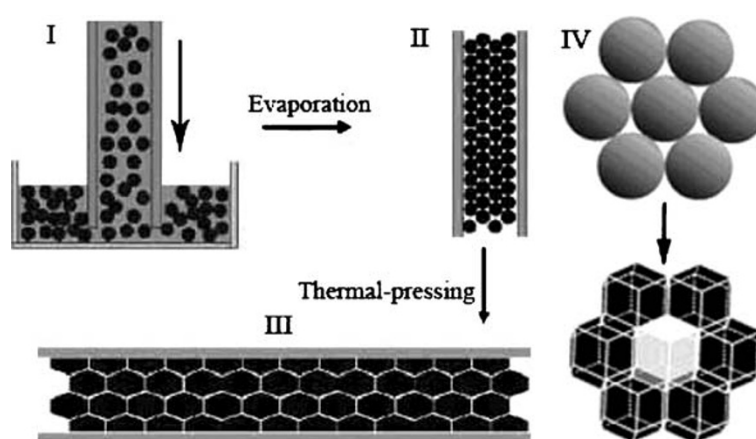
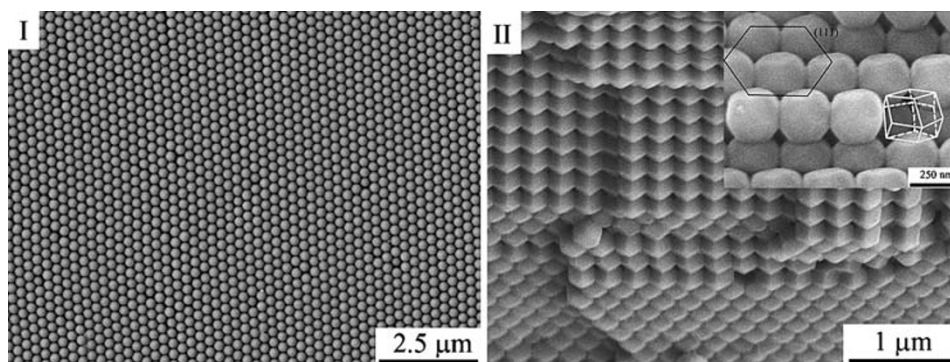


Fig. 2 SEM images of the colloidal crystals fabricated by two-substrate vertical deposition (**I**) and of the NSCCs (**II**). The inset in (**II**) is high magnification SEM image of the NSCCs



would extrude air in the interstices and dominated the deformation process smoothly and swiftly. Moreover, the temperature lower than T_g of polymer microspheres prevented colloidal crystals from fusing into membrane. Figure 2II shows the section SEM image of the NSCCs, and its inset shows the high magnification SEM image of the inner layers view at a tilt angle of 45° to the normal of the (111) plane. As compared with spherical colloidal crystals, the NSCCs should have different optical properties due to their special symmetry, which may be attractive in applications such as photonic crystals [50].

Colloidal crystals with ordered voids

Combining micro-contact printing (μ CP) [52], self-organization of organic liquid on patterned self-assembled monolayers (SAMs) [53], and vertical deposition [27–29], we have developed a simple method to fabricate ordered voids in a colloidal crystal film-substrate system [40]. Figure 3 outlines the procedure used to fabricate ordered voids in the colloidal crystal film. Gold-coated substrates were patterned with a hydrophobic SAM of hexadecanethiol and a hydrophilic SAM of mercaptopropionic acid by μ CP. When the patterned substrates were lowered through the interface between hexadecane and an aqueous solution, the hexadecane cannot wet the hydrophilic regions, while self-organized into droplets loaded on the hydrophobic regions, to minimize interfacial liquid energies. Figure 4I, III shows optical photographs of the organic liquid patterns (point and parallel lines) formed on the patterned gold substrates. Polymer microspheres were deposited on the

hexadecane-patterned gold substrates by vertical deposition. During the deposition process, the strong capillary force, formed at the meniscus between the substrate and the colloidal solution, drove the microspheres to assemble around hexadecane droplets into 3D close-packed arrays. Once the crystallization was finished, hexadecane evaporated through the interstitial spaces between the spheres, resulting in ordered microstructures of voids between the crystal films and the gold substrates. Figure 4II, IV shows SEM images of colloidal crystal films with point- and line-like voids, derived from templates shown in Fig. 4I and III, respectively. These voids are potentially useful as optical cavities and waveguides for light in photonic chips. Besides the voids shown in Fig. 4, more complex microstructures may be produced by rationally designing the structures of the organic liquid templates.

Patterned colloidal crystals

Applying lift-up soft lithography [63] and μ CP to colloidal crystallization, we have developed versatile approaches to patterned colloidal crystals of various structures. As illustrated in Fig. 5I, a PDMS stamp with patterned features was brought into contact with the colloidal crystal film deposited on a silicon substrate. After the sample was heated at 100°C for 3 h and the PDMS stamp was carefully peeled away, a single layer of close-packed microspheres was transferred to the surface of PDMS stamp and the corresponding pattern was formed on the colloidal crystal film surface. Figure 6I shows a typical SEM image of parallel lines of 2D colloidal crystalline arrays fabricated by a one-step lift-up process. We also tried to

Fig. 3 Schematic illustration of the procedure used to fabricate ordered voids in the colloidal crystal films

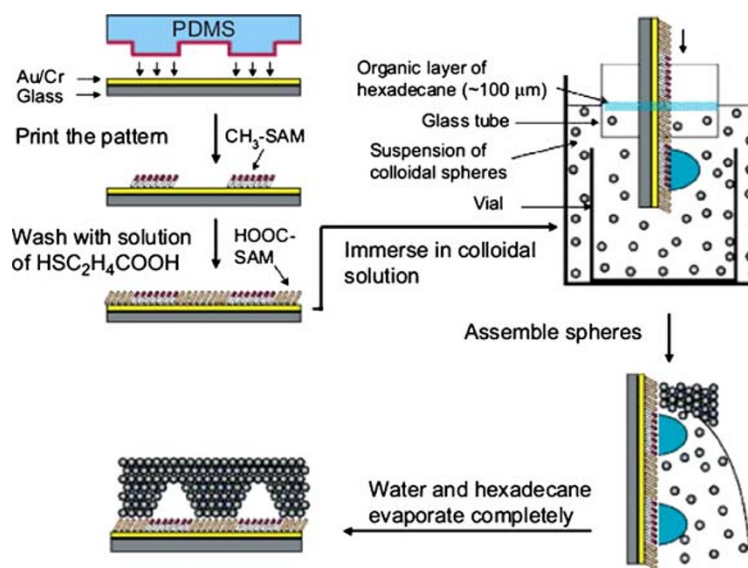
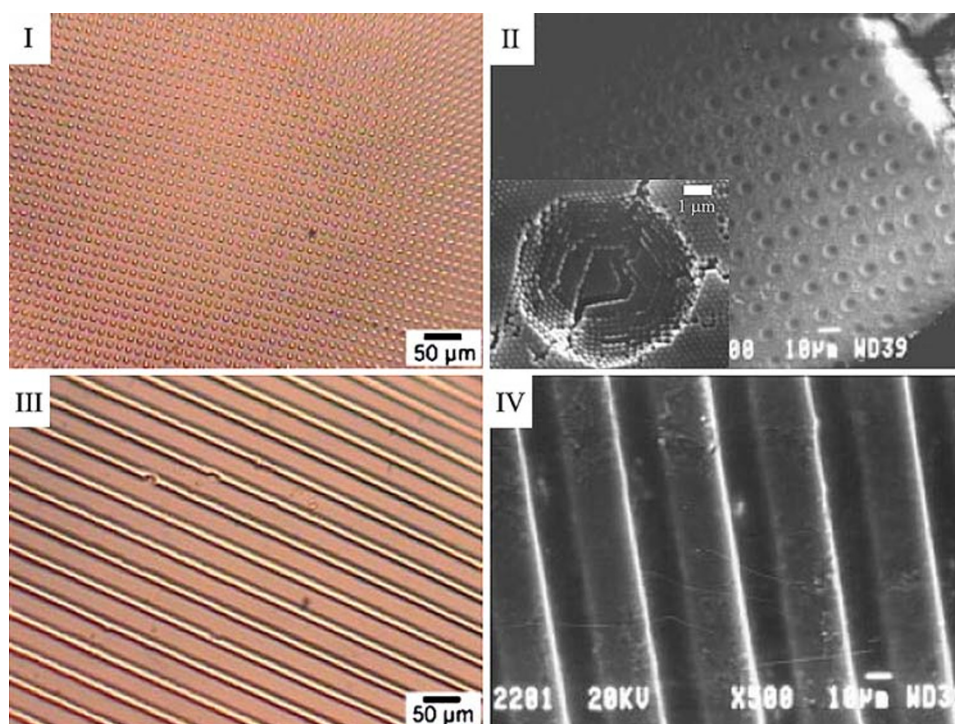


Fig. 4 (I, III) Optical photographs of the organic liquid patterns. **(II, IV)** SEM images of colloidal crystal films with point- and line-like voids derived from templates shows in **(I, III)**. The inset in **(II)** is high magnification SEM image of the voids in colloidal crystal films



apply this method to prepare microstructures of 3D colloidal crystalline arrays. Figure 6II shows the resulting microstructures in a double-layered crystal film fabricated by a two-step lift-up process. First, a single layer of the microspheres was selectively removed, leaving parallel lines in the top layer. Second, another PDMS stamp with the same patterned feature was applied to this patterned crystal film in a direction orthogonal to the initial stamp orientation, under a high pressure of 1.0×10^5 Pa. Ordered squares of colloidal crystals were formed in the top layer and ordered squares of voids appeared in the second layer. This method is versatile not only for patterning the colloidal crystals on substrates, but also for selectively

creating a single layer of ordered microspheres on the protruding surface of a PDMS stamp. A stamp with features of micrometer-sized hemispheres was used to transfer microsphere arrays in lift-up lithography, fabricating micrometer-sized hemispheres covered with hexagonal close-packed (hcp) silica microspheres, (Fig. 6III). This special structure would be potentially useful as a model system to develop optical designs with ultrawide fields-of-view.

Based on lift-up lithography and μ CP, we have succeeded in transferring colloidal crystals intentionally [42]. As shown in Fig. 5(II), a thin film of polymer, usually poly(vinyl alcohol) (PVA) was either spin-coated on planar substrates or dip-coated on

Fig. 5 Schematic illustration of lift-up soft lithography **(I)** and μ CP **(II)** of colloidal crystals

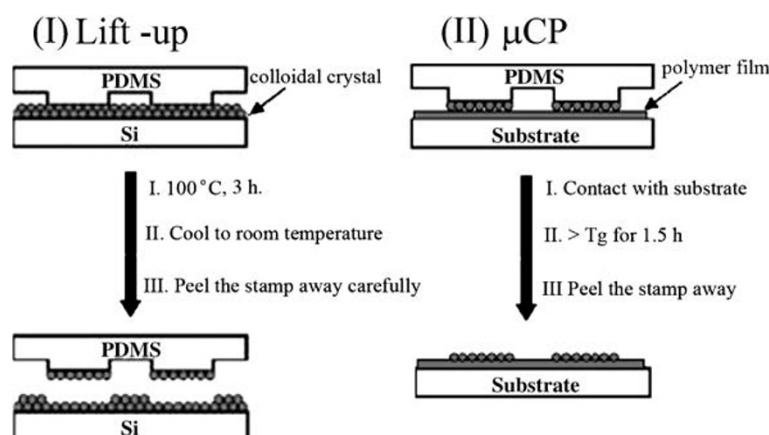
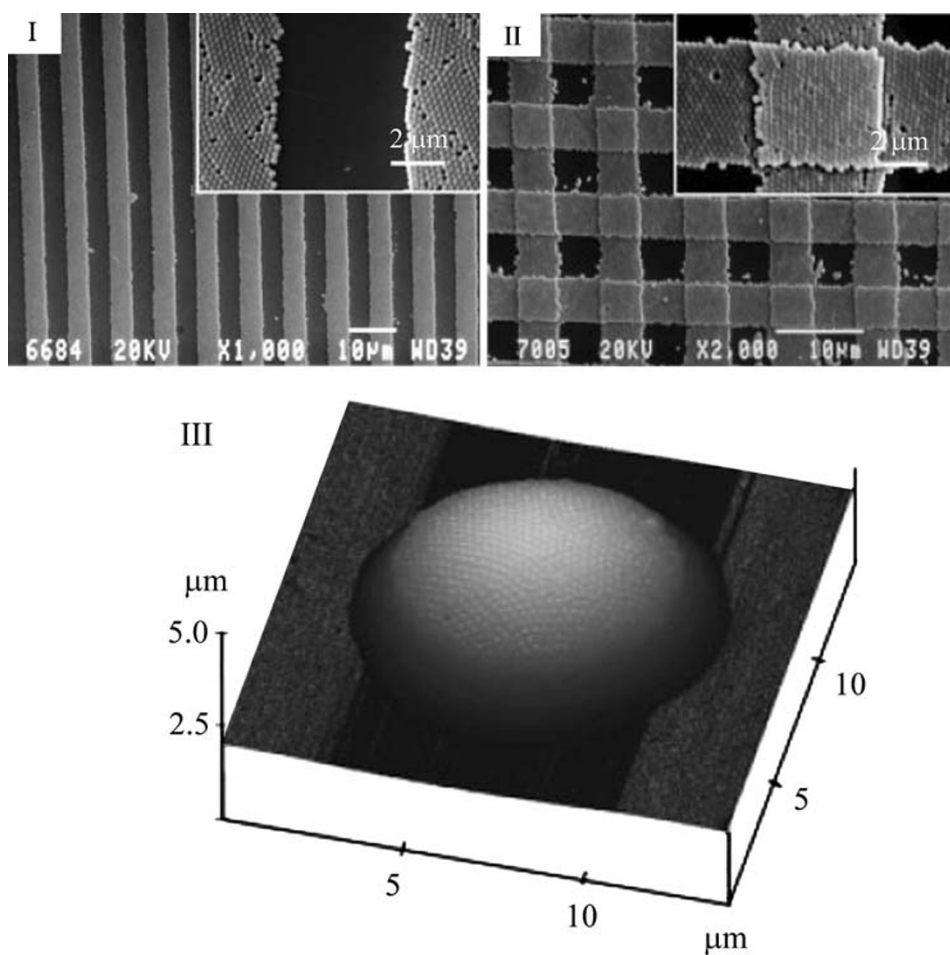


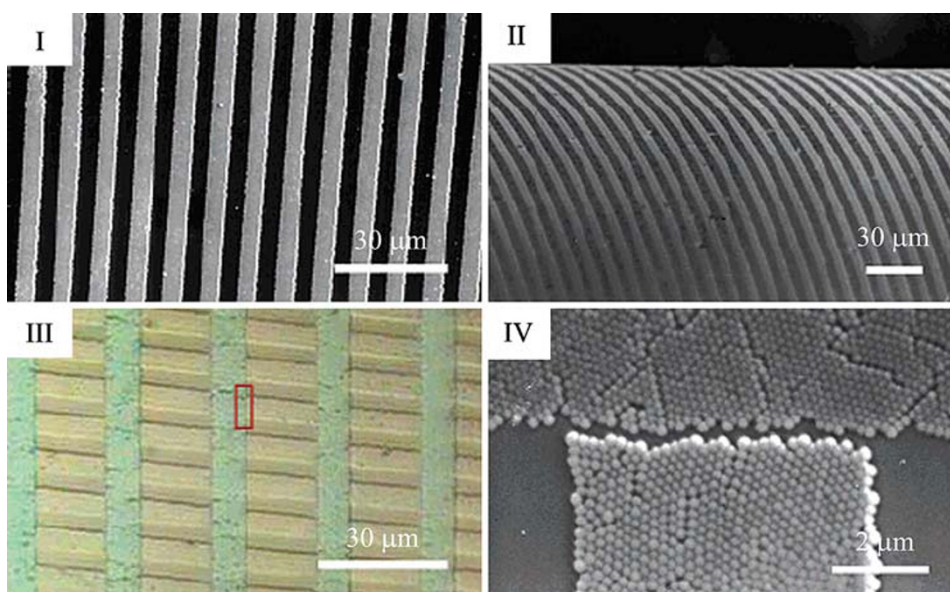
Fig. 6 (I, II) SEM images of 2D and 3D patterned colloidal crystals fabricated by lift-up process. (III) 3D AFM image of micrometer-sized hemisphere covered with hcp silica microspheres



non-planar substrates. The PDMS stamp coated with 2D colloidal crystal films was brought into contact with the PVA film. After the sample was heated above T_g

of PVA for a while, the PDMS stamp was peeled off carefully, and the 2D colloidal crystal films were transferred onto the substrate. Figure 7I, II shows the

Fig. 7 (I, II) SEM images of the patterned 2D colloidal crystal on planar and non-planar substrates. (III) Optical photograph of the patterned heterogeneous colloidal crystal using a two-step μ CP procedure. (IV) High magnification SEM image of a crossover of two crystal film lines in (III)



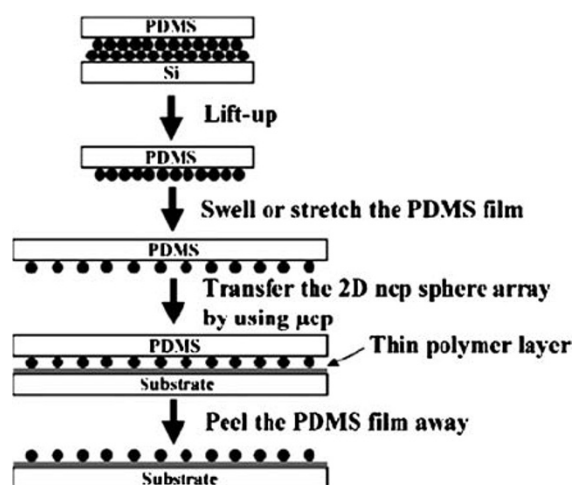


Fig. 8 Schematic illustration of the procedure for fabricating 2D ncp array of microspheres

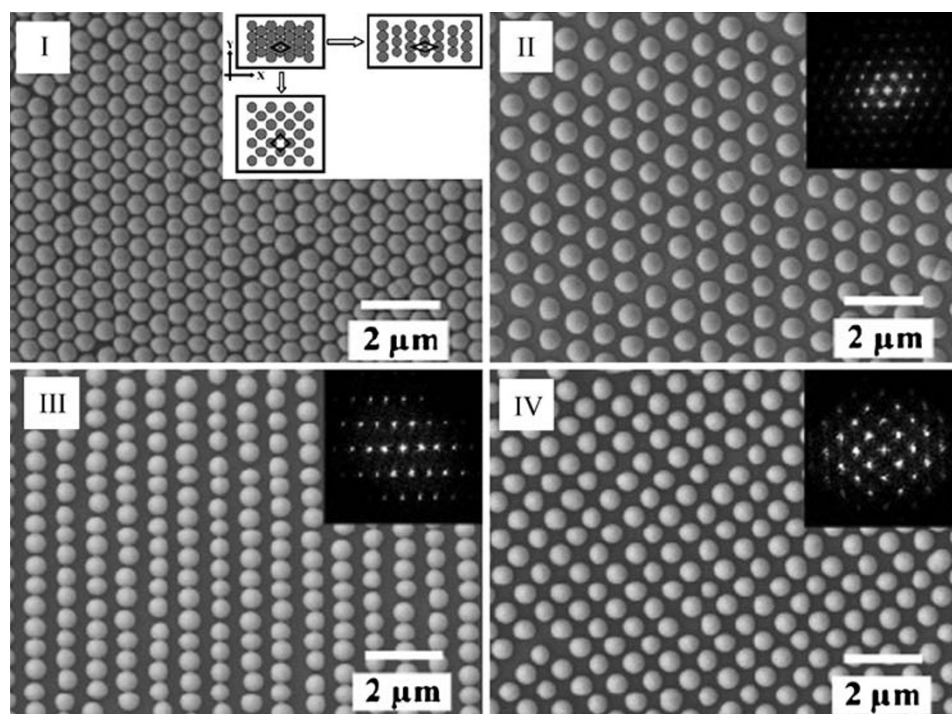
SEM images of the patterned 2D colloidal crystals formed on planar and non-planar substrates. Our method is versatile not only for patterning colloidal crystals on both the planar and non-planar substrates, but also for creating the heterogeneous crystal film. For example, Fig. 7III shows an optical photograph of the patterned heterogeneous colloidal crystal constructed from two different microspheres, which was fabricated via a two-step μ CP procedure. In the first step, a single layer of close-packed polystyrene (PS) microspheres was transferred onto a substrate using the procedure

outlined above. Then a silica microsphere-coated stamp with different relief structure was applied to the primary patterned colloidal crystal film in a direction orthogonal to the initial stamp orientation. The lines of heterogeneous colloidal crystalline arrays in the resulting pattern show two kinds of uniform colors due to light diffraction. The high magnification SEM image (Fig. 7IV) of a crossover of two crystal film lines displays the heterogeneous structures of this colloidal crystal: one line is made of 230 nm silica microspheres, and the other is made of 200 nm PS microspheres.

Non-close-packed arrays of colloidal microspheres

It is well-known that conventional self-assembly methods could be applied to produce 2D or 3D ordered arrays of colloidal microspheres. Using etching techniques [54, 55] or charged spheres [56], non-close-packed (ncp) arrays with controllable spacing between spheres can be created. Nonetheless, it is difficult to obtain lattice structures different from hexagonal packing. As mentioned in the last part, we have demonstrated a lift-up soft lithography technique to form 2D hcp microsphere arrays on the surface of PDMS stamp [41]. Based on the solvent-swelling [57] and mechanical deformation behaviors of PDMS, we can adjust the lattice structures of these 2D microsphere arrays [44]. Most importantly, the as-prepared 2D ncp arrays can be transferred onto the surfaces of solid

Fig. 9 SEM images of the close-packed array of silica microspheres (I), hexagonal ncp arrays fabricated by swelling (II) and ncp microsphere arrays with new lattice symmetries resulted from stretching (III and IV). Inset in (I) illustrates two typical crystal lattices of ncp microsphere arrays obtained by stretching. Insets in (II, III and IV) display the Fourier transforms of the corresponding images



substrates by using a modified μ CP transfer technique [42]. The experiment procedure is illustrated in Fig. 8. By using the lift-up soft lithography, a single layer of hcp microspheres were transferred to the surface of PDMS film, which was subsequently stretched or swollen with a mixture of toluene and acetone to transform the hcp arrays into the ncp ones. The 2D ncp arrays obtained on the deformed PDMS film were transferred to a PVA-coated substrate by the modified μ CP technique. Figure 9I shows a typical SEM image of the hcp ordered silica microsphere array. Figure 9II displays an ordered 2D hexagonal ncp array of microspheres transferred to a polymer-coated substrate by using a PDMS film swollen with pure toluene. By stretching the microsphere-coated PDMS elastomers, ncp arrays with new crystal lattices were obtained. Inset in Fig. 9I schematically illustrates two typical crystal lattices of the ncp microsphere arrays resulted from stretching. Figure 9III shows an SEM image of the quasi-one-dimensional parallel wires of silica microspheres that were fabricated by stretching the PDMS film along x -axis by about 163% while maintaining the length of y -axis. Figure 9IV shows an SEM image of the square ncp structure formed by stretching the PDMS film along y -axis by about 166% while maintaining the length of x -axis. As a result of the controllable homogeneous macroscopic elongation of PDMS film, the hcp arrays can be transformed into various ncp lattices. Although the crystal lattices are greatly changed, the long-range ordering are essentially preserved in the resulting ncp arrays, which can be evidenced by Fourier transforms of the corresponding images displayed in the insets.

In brief, using the solvent-swelling and mechanical deformation behaviors of PDMS elastomers, we have

developed a simple soft lithography technique to fabricate ncp microsphere arrays with designable lattice structures. This technique provides a simple and flexible route for creating microlens arrays [56, 58] and adjustable templates for the systematic study of the epitaxial growth of 3D colloidal crystals [59, 60], and for the fabrication of novel nanostructures, such as ordered arrays of nanoholes [61] or nanodots on various substrates.

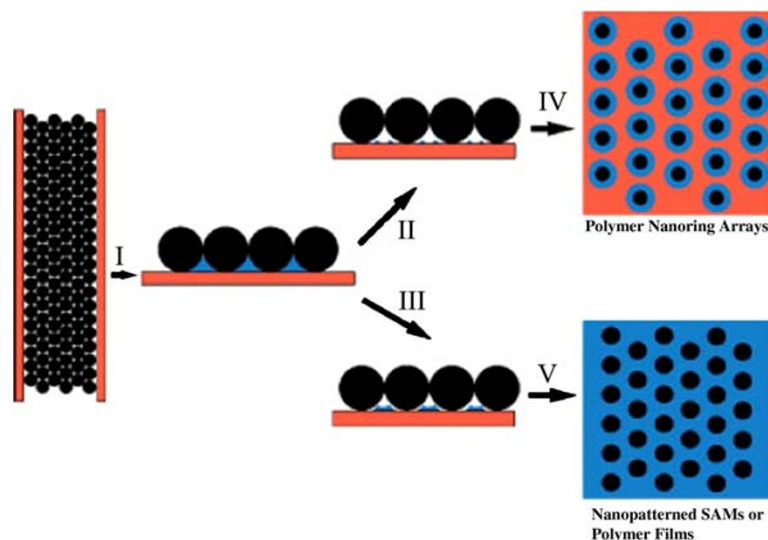
Application of colloidal crystals as templates for surface patterning

A number of approaches, involving μ CP and soft lithography [62, 63], self-assembly, and laser-assisted directed imprinting lithography [64], have been applied to pattern surfaces. However, to achieve 2D nanopatterned SAMs and desired morphologies on various substrates remains a challenge. Using the colloidal crystals as templates, we have developed a number of methods to generate surfaces patterned with different structures range from nanoscale to micron-scale. Particularly, we have developed colloidal-crystal-assisted-capillary nanofabrication (CCACN) [45] and colloidal-crystal-assisted-imprint (CCAIP) [46] techniques, in which we intentionally applied 3D colloidal crystals in preparing 2D nanostructures on various substrates.

CCACN approach to 2D nanostructured surface

Figure 10 outlines the procedure of CCACN approach. In step (I) a solution of polymer or reagents, which could react with the substrates, was penetrated into the

Fig. 10 Schematic illustration of the CCACN



interstices in colloidal crystal chips obtained by two-substrate vertical deposition, followed by drying in air. Steps (II) and (III) show the dewetting or the reaction of the filling species, solutions with a low and high concentration, respectively. Steps (IV) and (V) involve the ultrasonication and rinsing to remove the microsphere templates. Figure 11I, II shows typical 3D AFM images of PVA nanostructures fabricated by infiltrating aqueous PVA solution of 10 mg/mL and 40 mg/mL, respectively.

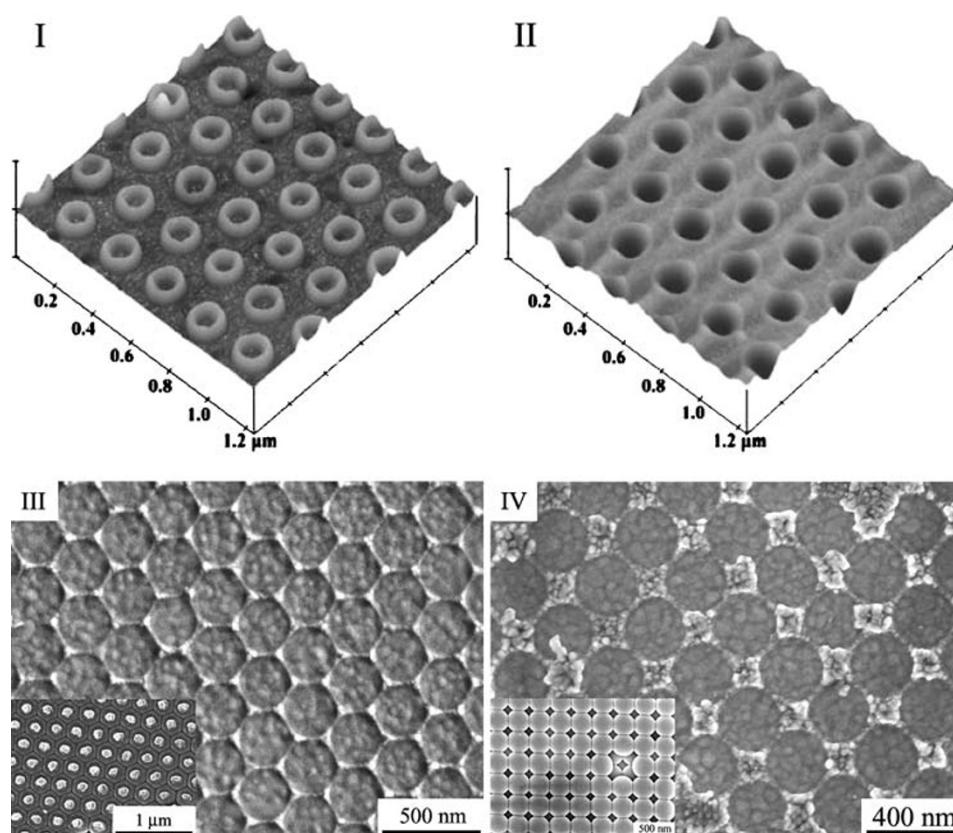
When we change the spherical colloidal crystal templates to non-spherical ones, nanostructures with different symmetry can be fabricated accordingly. For the NSCC obtained by pressing, there is a flat surface on the side adhered to the substrate. Insets in Fig 11III, IV show the morphology of the NSCCs surfaces adhered to the substrates. These two NSCCs are of different crystalline orientations. Using these NSCCs as templates in CCACN, 2D nano-networks can be obtained (Fig. 11III, IV). First, NSCCs were fabricated between two gold-coated wafers by the method mentioned above. Second, we dipped as-prepared NSCCs chips into a solution of silver enhancer (1:1 A/B), the solution was sucked into the interstices in the NSCCs. After reacting for 30 min at room temperature, the

silver enhancer formed silver patterns on the bare surfaces of the gold substrates, which were not covered with polymer particles. By removing the polystyrene particles with toluene, silver structures were left on gold wafers. Since we can adjust the structures and size of colloidal crystal chips and the chemical nature of substrates, our method can be readily to extend to other materials, opening up a variety of applications in nanofabrication, nanosensors, microreactors, and the control of crystallization.

CCAIP approach for mesoscopic structured arrays and hierarchical patterns

Using 3D self-assembled colloidal crystals as masters in mesoscopic imprint lithography, CCAIP approach is generally applicable. Figure 12 outlines the CCAIP procedure for patterning polymer or multilayered hybrid films. First, the substrates were coated by polymers or multilayered hybrid films by spin-coating or chemical vapor deposition (CVD). Second, colloidal crystals of silica microspheres were formed between two desired substrates by two-substrate vertical deposition (I). Third, the colloidal crystal chips were imprinted at a temperature above T_g of the polymer

Fig. 11 (I, II) Typical 3D AFM images of PVA nanostructures fabricated by CCACN. (III, IV) SEM images of silver nano-networks on gold substrates with different symmetries. Insets in (III) and (IV) show the SEM images of the non-spherical templates used to obtain the nano-networks shown by corresponding images



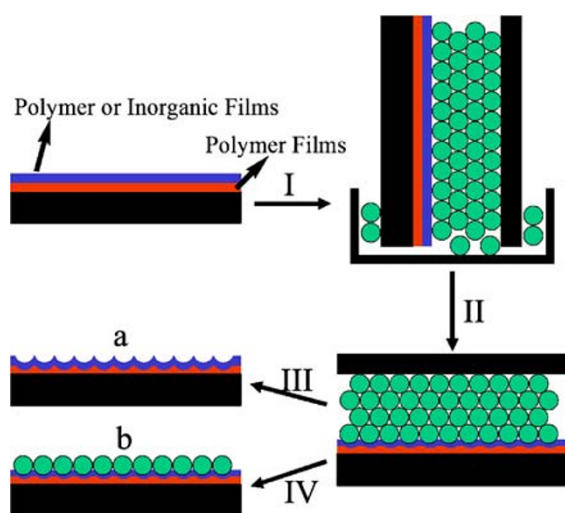


Fig. 12 Schematic procedure of CCAIP for patterning polymer or multilayer hybrid films

(II). Finally, 2D-patterned structures were achieved on the substrates after the removing of the 3D colloidal crystals by chemical etching (III) or ultrasonication (IV).

Figure 13I shows an array of pores in polystyrene film coating on gold-coated substrate. The pore walls' thickness is 20–50 nm, their periodicity about 290 nm, and their depth 120 nm. Figure 13II presents the SEM image of a patterned surface with hierarchical mesoscopic hybrid structures. We obtained this complex patterned surfaces by spin-coating a layer of polymer film onto a silicon wafer, followed by depositing a gold film on it, then combining the hybrid-film-coated silicon wafer with a patterned PDMS stamp to carry out the CCAIP procedure. In this case, we removed the 3D colloidal crystals by ultrasonication, and many microspheres were left on the substrate (as illustrated by Fig. 12b) generally according to the protruding structure of PDMS stamp. Although we have not yet quantified the accuracy in hierarchical registration, it

Fig. 13 (I) SEM image of pore arrays in a polystyrene film coated on gold substrate. (II) SEM images of patterned surfaces with hierarchical mesoscopic hybrid structures. The insets are high magnification SEM images

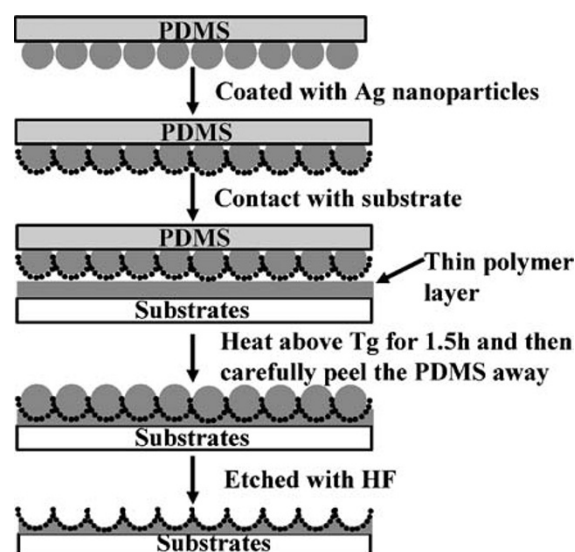
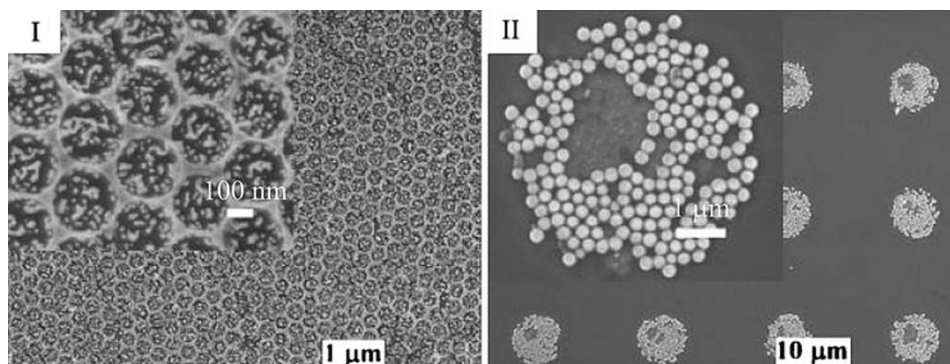


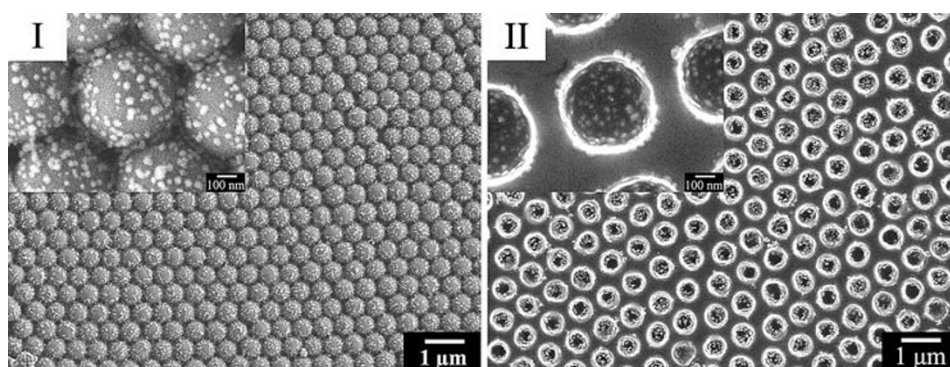
Fig. 14 Schematic illustration of the procedure used to prepare ordered silica microspheres unsymmetrically coated with Ag nanoparticles and Ag-nanoparticle-doped polymer voids

can be expected to extend to other materials and various applications in nanofabrication, hierarchical patterns, and hybrid plastic electronics.

Ordered silica microspheres unsymmetrically coated with Ag nanoparticles and Ag-nanoparticle-doped polymer voids

The design and preparation of unsymmetrically coated colloidal particles have been a long-standing challenge in surface and colloid science [65–69]. Based on the lift-up soft lithography of colloidal crystals [41], we developed an alternative way of fabricating ordered silica microspheres unsymmetrically coated with Ag nanoparticles by chemical reduction [47]. Taking advantage of the flexibility of μ CP technique [42], these microsphere arrays can be easily transferred onto polymer-coated solid substrates and precisely realize a

Fig. 15 (I) SEM image of ordered silica microspheres unsymmetrically coated with Ag nanoparticles. (II) SEM image of the ordered Ag-nanoparticle-doped polymer voids. The insets are high magnification SEM images



tropism conversion. By etching away the silica microspheres, ordered Ag-nanoparticle-doped polymer voids are obtained.

Figure 14 outlines the procedure for preparing ordered silica microspheres unsymmetrically coated with Ag nanoparticles and Ag-nanoparticle-doped polymer voids. First, a single layer of close-packed silica microspheres are transferred onto the surface of a PDMS stamp by using the lift-up soft lithography technique. After depositing Ag nanoparticles on the microspheres by chemical reduction [39], the silica microspheres are unsymmetrically coated with Ag nanoparticles, which can be transferred onto another substrate by a μ CP technique. By etching away the silica microspheres with hydrofluoric acid, ordered Ag-nanoparticle-doped polymer voids are finally obtained. Figure 15I is an SEM image of ordered silica microspheres unsymmetrically coated with Ag nanoparticles on the PDMS stamp. The silica microspheres are uniformly coated with Ag nanoparticles and also adopt an ordered hexagonal array. Due to the uniformity of the Ag nanoparticles and the ordered arrays of the composite microspheres, these ordered microspheres can be used as substrates for surface-enhanced Raman scattering (SERS). Figure 15II is the SEM image of the ordered Ag-nanoparticle-doped polymer voids after the silica microspheres are etched away.

Conclusion

In conclusion, we have demonstrated a set of approaches to fabricate new colloidal crystals with ordered voids, 2D- or 3D-patterned arrays, composed of non-spherical polyhedrons, patterned colloidal crystals on non-planar surfaces, heterogeneous colloidal crystals of different building blocks, and particularly colloidal crystals of non-close-packed colloidal microspheres. These new colloidal crystals should be of importance in a wide range of applications, especially

in photonics. Using various colloidal crystals obtained as templates, several methods have been established to generate surface patterns with different structures range from nanoscale to micron-scale. Particularly, we have put up CCACN and CCAIP techniques, in which we intentionally applied 3D self-assembled colloidal crystals in preparing 2D nanostructures on different substrates. Therefore, our methods listed here should hold immersed promise in nanofabrication, nanosensing, microreactors, and control of colloidal crystallization.

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